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AN EVALUATION OF ETCHANTS AND TECHNIQUES USED TO PRODUCE DISLOCATION ETCH PITS ON NaCl

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A comparison of the six most commonly used etchants for NaCl has been made together with an evaluation of various etching and observation techniques. All six etchants were found to produce usable pyramidal etch pits when special techniques were employed. A one-to-one correspondence in number and location has been established for the etch pits produced by all six etchants. On the basis of this correspondence, the only advantage in using one etchant in preference to another to study dislocations in NaCl appears to be ease of observation.

INTRODUCTION

The successful use of etch pits to study dislocations in NaCl single crystals depends appreciably on the etchant and experimental techniques employed. In view of the many recently developed etchants for NaCl and the number of reported comments concerning the etching of this material[1-4], a comprehensive evaluation was undertaken. The purpose of the work reported here was to make a comparison of six of the most commonly used NaCl etchants and an evaluation of various techniques employed.

THE ETCHING TECHNIQUE

To properly make a study of etchants, all variables except the action of the etchant should be held constant. Such variables as dislocation

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density, cleavage damage, and purity are difficult to hold constant, but other factors can be controlled by adopting good techniques. A standardized technique was arrived at after investigating the phases of the etching and observation process. The results of this investigation are given first since this was prerequisite to studying the etchants.

Handling. - During the etching and observation process manipulation of the specimen is obviously essential. This manipulation must be accomplished in a manner such that dislocations are not generated or caused to move. This is an especially difficult task in the case of NaCl because dislocations in this material can move at stresses below 25 g/sq mm[5] and such stresses can be generated by forceps, fingers, or other conventional holding devices. Successive etching of a single specimen or the matching of etched cleavage halves shows that even the most careful handling of the specimen produces unwanted effects. For example, fig. 1 shows the movement of dislocations produced by holding the specimen with Teflon-coated forceps during etching. Also, from fig. 2 it can be seen that there is not an exact correspondence between etch pits on the cleavage halves and the differences might possibly be due to the way each half was handled, even though extreme care was exercised.

A technique for manipulating specimens, found to be superior, consists of cementing the specimen to a glass slide. Once the specimen is affixed to a slide it can be manipulated without direct contact, and any area can quickly be relocated by noting the coordinates from a mechanical stage. For cementing the specimen to its "handle", Eastman 910 Adhesive[6] has proved most suitable because (1) no heat or pressure are required to facilitate the cure, (2) no shrinkage occurs upon curing, (3) the cement is insoluble in all etchants and rinses employed, and (4) an excellent bond is attained in seconds.

Polishing. - The polishing of NaCl surfaces to be used in dislocation etch pit studies requires a solvent whose surface dissolution rate is low enough to allow controlled removal of surface material. Water is unsatisfactory because its dissolution rate is much too high, and other solvents in which NaCl is less soluble (e.g., alcohols) produce slight etching action. Hydrochloric acid when diluted with water produces suitable dissolution rates without causing etching. When used with slow, rocking agitation, a solution of one part water and four parts concentrated hydrochloric acid has a surface dissolution rate of 1μ/min. Other rates can be attained by changing the concentration.

Post-etch rinsing, drying, and storing. - As expected, the etched surface of a highly water-soluble material, such as NaCl, becomes marred by exposure to excessive moisture and as Mendelson has shown,[2] the etch pits on NaCl are all but obliterated by high humidity. Consequently, care must be taken to protect the etched surface, and this care necessarily begins with the post-etch rinsing. The rinse must remove the etchant without adding water to the surface. Water can be added to the surface if the rinse has a strong tendency to absorb water or if it evaporates so rapidly that it cools the surface sufficiently to cause condensation. Many rinses have been suggested, namely, pyridine,[4] petroleum ether,[3] carbon titrachloride,[1] and acetone,[2] but acetone possesses the advantages of mild odor and low toxicity. Acetone does not absorb sufficient water to cause marring of the etched surface and its rate of evaporation is low enough not to cause condensation.

Drying with forced or hot air requires extreme caution because of the possibility of causing thermal shock. When acetone is used as a post-etch rinse, forced drying is not required. Successive etching experiments have not revealed etch pits that could be attributed to thermal shock caused by rapid evaporation of the acetone.

Etched NaCl specimens, rinsed with acetone, have been stored for up to one month under a watch glass in a dessicator or for up to one year in stoppered vials. The etch pits on these specimens were still of good quality, and these specimens photomicrographed as well as those done immediately after etching.

Observation. - The particular observation mode used to view etch pits depends on (1) the type and quality of etch pits and (2) the micrographic equipment available. For almost all etch pits ordinary bright-field illumination is unsatisfactory because it does not yield sufficient contrast to clearly reveal all etch pits. Generally, oblique incident illumination is most suitable and the shallower the etch pits the more oblique the illumination required. For very shallow etch pits or for high magnifications, sufficiently oblique illumination is difficult to obtain without special equipment, such as the Leitz Ultropak.[7] When such equipment is not available, incident light phase contrast or other interference techniques can be used with various degrees of success as shown in figs. 3 and 4, respectively.

With a little adjustment, the conventional metallurgical microscope can be used to observe several types of etch pits produced on NaCl. By closing down the aperature diaphragm and moving it off center slightly, a degree of oblique illumination can be obtained that produces adequate contrast up to magnifications of approximately ×450. Of course this procedure results in some loss of uniformity of illumination over the entire field of view, and hence nonuniform negatives result when photographs are being taken.

As far as observation of etch pits is concerned, there is no substitute for sharpness and a suitable depth to width ratio. A depth to width ratio of 0.15 is optimum.

COMPARISON OF ETCHANTS

Table I lists the six etchants investigated together with a comparison of the etch pit properties associated with the respective etchants. Detailed results of this phase of the investigation are presented below.

Anhydrous methyl alcohol produces by far the shallowest etch pits and etching times as short as one second still result in etch pits that are very difficult to observe. Figure 3 is a phase contrast view of methyl alcohol produced etch pits on NaCl; with bright field illumination these pits are not recognizable. Also, when methyl alcohol is used as an etchant, so much dissolution takes place that many shallow dislocation half loops are etched completely out of the specimen and all etch pits overlap to such an extent that a confusing scene results.

Moran's NaCl etchant[1] produces greater dissolution and shallower etch pits than the etchants based on acetic or propionic acid, but good quality pits can be obtained with etching times of from 10 to 40 seconds as shown by fig. 5. While additions of 1 to 2 percent water to the etchant results in shorter etching times and shallower etch pits, the excessive sensitivity at atmospheric variables (viz., relative humidity) reported in the literature[2,3] has not been noted. Letting the etchant stand for several hours in an open vessel on a day when the relative humidity was 90 percent did not alter the etching time or quality of the etch pits produced.

The etchants of Mendelson[2] and Barber,[4] based on acetic acid, produce the best quality etch pits for ease of observation and etching times of about 30 sec sum to be optimum. Mendelson's observations regarding small quantities of water in the etchant have been found to apply equally to Barber's etchant; water reduces the etching time and produces a shallower pit with some rounding of the pit's edges.

Moran's KCl-KBr etchant,[1] when used on NaCl with etching times of from 15 to 25 sec, produces a shallow etch pit that requires very oblique illumination for viewing. This etchant possesses a serious disadvantage in that during the etching process crystallization takes place on the surface, and this greatly hinders observation of the etch pits. By diluting this etchant with an equal volume of 95-percent ethyl alcohol, crystallization on the surface is minimized without affecting the etch pits. At best, however, only small areas are free from crystallites and this limits the usefulness of this etchant.

Cook's etchant[3] based on propionic acid produces well-defined etch pits on NaCl. Best results were obtained with this etchant when etching times of 40 seconds were employed. Like the other etchants investigated, this etchant was found to produce shallower etch pits when water was added.

All six etchants investigated were found to etch fresh and aged dislocations equally well. Amelinckx has reported[8] that methyl alcohol attacks the "grown in" dislocations somewhat better, but in this study no such preferential action was detected.

Barber in his figs. 2(a) and (b)[4] shows matching cleavage faces (of a material not specified) etched with his etchant and a Moran etchant, respectively. From Barber's figure it is readily seen that the etch pits produced by the Moran etchant have the edge of their base inclined 45 deg to the edge of the base of the etch pits produced by Barber's etchant. (Hereafter the edge of the base of the etch pits will be used to define the orientation of the etch pits.) Barber gives the orientation for the etch pits produced by his etchant as [100] (i.e., the edge of the base is parallel to [100] directions) and the orientation of the etch pits produced by Moran's etchant as [110]. In the reference cited by Barber, Moran describes etchants for NaCl, KCl-KBr, and KI, respectively, and Barber does not state specifically which of these etchants he employed. Moran's NaCl etchant produces etch pits with a [100] orientation. Figure 5 shows a NaCl cleavage face etched with Moran's NaCl etchant together with a [100] edge of the specimen; it can be seen from fig. 5 that the etch pits have a [100] orientation. Furthermore, fig. 2 shows matching cleavage faces of NaCl etched in Barber's and Moran's NaCl etchant, respectively, and it will be noted that each set of etch pits is identically oriented. The etch pits produced by Moran's KCl-KBr etchant were found to have a [110] orientation, and presumably this is the etchant Barber used to obtain his fig. 2(b).

In the course of this investigation, it was discovered that if absolute ethyl alcohol (instead of 95 percent) and anhydrous $BaBr_2$ were used to compound Moran's KCl-KBr etchant, the etch pits produced by this "dry" etchant had a [100] orientation. Since $BaBr_2$ is quite insoluble in absolute ethyl alcohol, it might be concluded that insufficient $BaBr_2$ went into solution to produce the [110] etching action; however, additions of about 2-percent water to the "dry" compounded etchant caused the desired [110] etching action, while higher saturation values of $BaBr_2$ had no effect. Apparently then the $BaBr_2$ concentration is not as critical in producing an etch-pit orientation as the presence of some water.

Figure 4 shows the cleavage face of a NaCl crystal first etched in Moran's KCl-KBr etchant for 30 sec, rinsed in acetone, and then immediately etched in Barber's etchant for 20 sec. (A Zeiss two-beam interference microscope was used in making this photograph.) From this figure remnants of the original [110] etch pit can be seen, and inside this can be seen the newly created [100] etch pit.

While the photograph of fig. 4 does show a few of what appear to be single-type etch pits, actual microscopic examination at a different focus and/or interference band interval, reveals that a [100] pit is always associated with each [110] remnant. Similar successive etching experiments have revealed that there is a one-to-one correspondence between the etch pits produced on NaCl by all six etchants studied.

Barber has pointed out[4] that Moran's etchant (presumably the KCl-KBr etchant) also produces some rounded etch pits not revealed by other etchants. Similar rounded etch pits have been observed on occasion when other etchants were used, but attempts to establish their correspondence to crystal imperfections have not been successful. At present it is felt that these rounded pits are an artifact of the etching process.

CONCLUSIONS

1. By employing suitable etching and observation techniques all six etchants investigated can be used to produce etch pits on NaCl.

2. The etchants based on acetic acid produce the most easily observed etch pits on NaCl.

3. A one-to-one correspondence between the etch pits produced by all six etchants has been established by the successive etching technique.

4. All six etchants produce etch pits at both fresh and aged dislocations.

5. On the basis of the one-to-one correspondence between etch pits produced by the various etchants and the fact that all etchants etch both fresh and aged dislocations equally well, there does not appear to be any advantage, besides ease of observation, in using one etchant in preference to another.

6. The fact that different etchants produce differently oriented etch pits implies that a difference in etching mechanism exists. Considering the etching mechanism proposed by Gilman, et al.,[9] based on the adsorption of cations at kinks, and simple geometric aspects of size, there appears to be no reason why different cations (e.g., Ba and Hg) of about the same size should produce differently oriented etch pits. Furthermore, the fact that the addition of water to Moran's "dry" compounded KCl-KBr etchant changes the orientation of the etch pits implies a more complex etching mechanism. Certainly further study along these lines is warranted.

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TABLE I. - A COMPARISON OF NaCl ETCHANTS

Etchant	Composition	Etching time, sec	Etch pit orientation (a)	Depth-to-width ratio (b)	Reference
Amelinckx	Anhydrous methyl alcohol	<1	[100]	0.050	8
Moran's NaCl	3 g $HgCl_2$ per liter absolute Ethyl alcohol	30	[100]	.100	1
Moran's KCl-KBr	95 parts Ethanol[c] 25 percent saturated with $BaBr_2$ 5 parts Methanol containing 100 g per liter $BaBr_2$	15	[110]	.070	1
Barber	50 parts Glacial acetic acid 1 part Hydrochloric acid saturated with $FeCl_3$ 1 part H_2O	30	[100]	.150	4
Mendelson	4 g $FeCl_3$ per liter Glacial acetic acid	30	[100]	.150	2
Cook	1.75 percent by weight $BaCO_3$ in propionic acid	40	[100]	.135	3

[a]Defined as direction parallel to base of etch pit.

[b]Determined with two-beam interference microscope.

[c]95-percent Ethyl alcohol.

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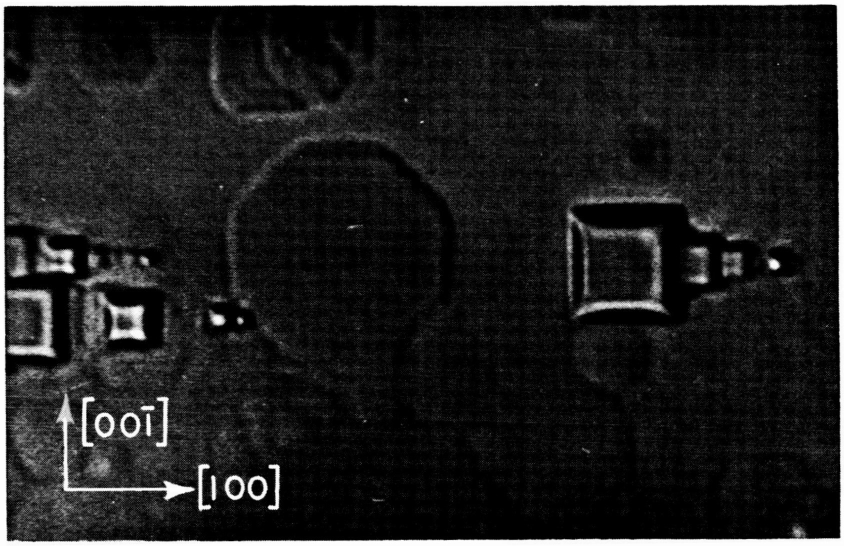

20 μ (10 mm) C-64410

Fig. 1. Etched NaCl surface showing movement of dislocations during etching process. Etched 30 sec in Moran's KCl-KBr etchant and 25 sec in Barber's etchant.

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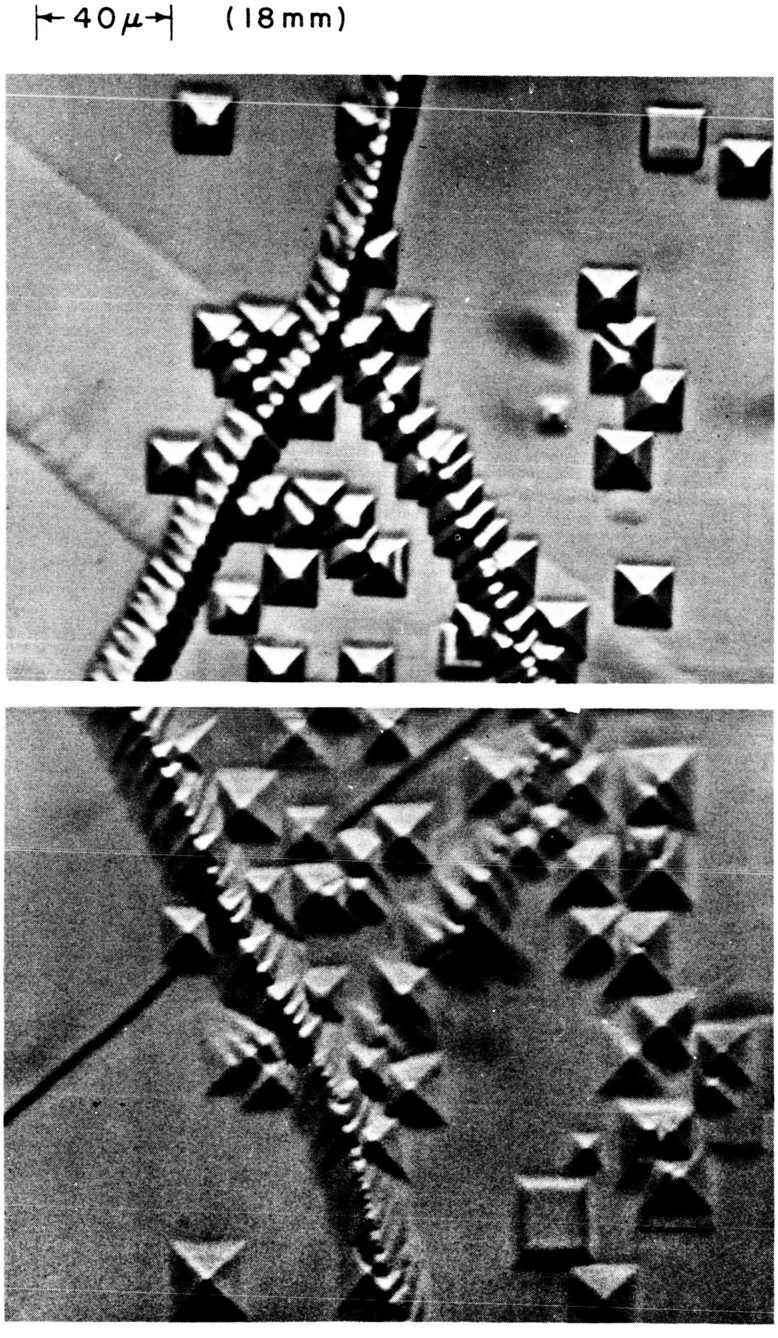
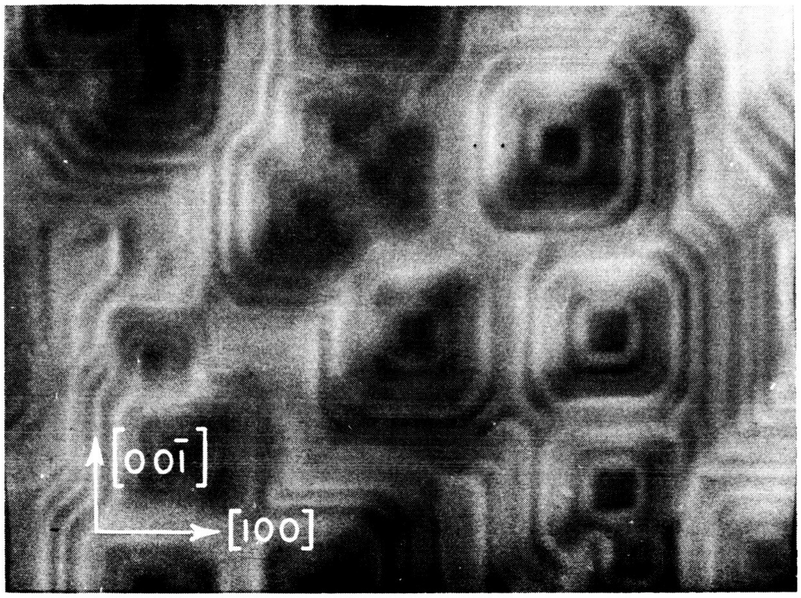


C-64411

(a) Barber's etchant for 30 sec.

(b) Moran's NaCl etchant for 50 sec.

Fig. 2. Cleavage halves of NaCl etched.



20 μ (10 mm)

C-64412

Fig. 3. Phase contract photograph of methyl alcohol produced etch pits on NaCl. Etching time, approximately 2 sec.

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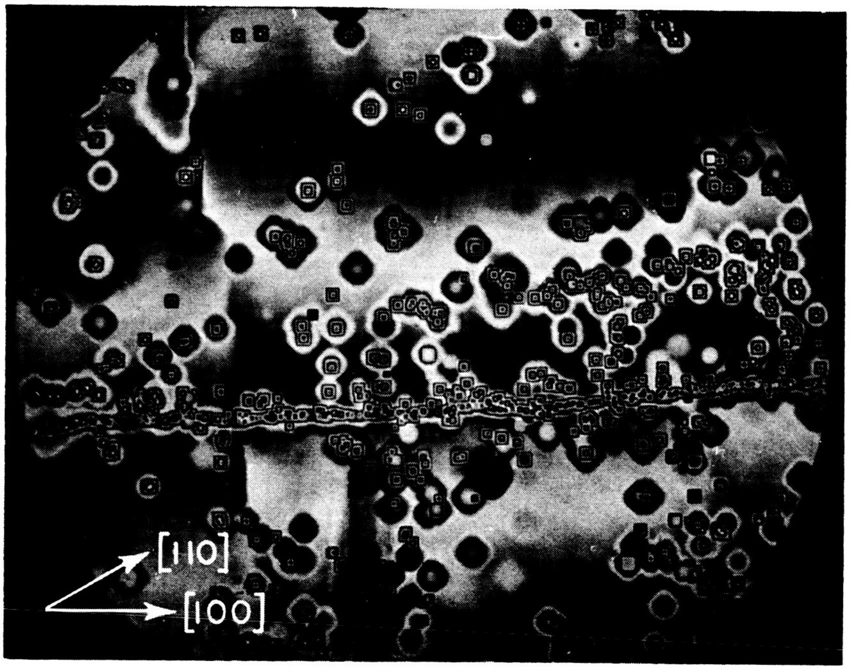

$\vdash$ 50 μ $\dashv$ (16 mm) C-64413

Fig. 4. Interference photograph of NaCl surface successively etched in Moran's KCl-KBr etchant for 30 sec and Barber's etchant for 20 sec.

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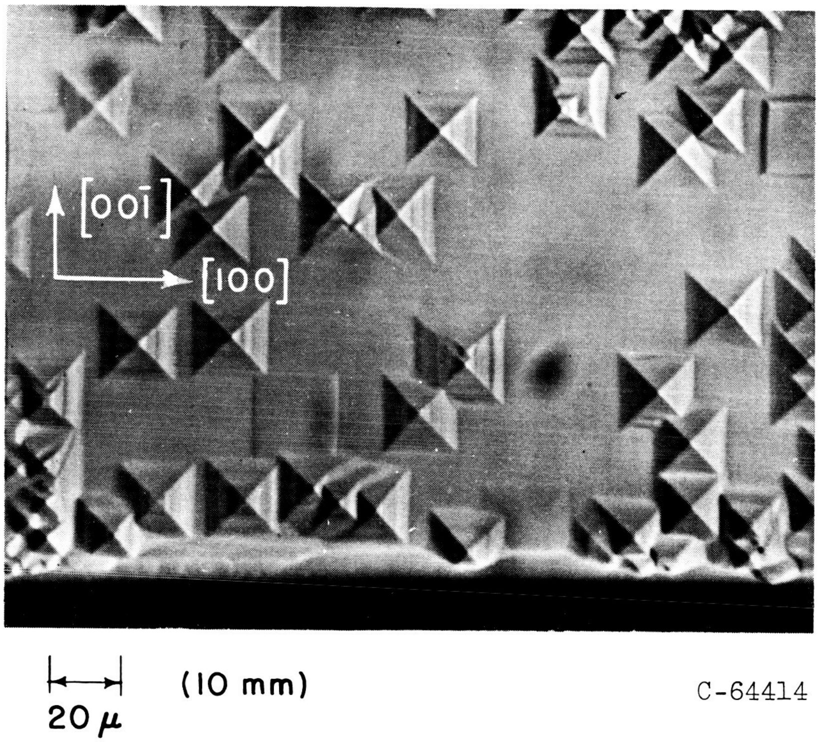

C-64414

Fig. 5. NaCl cleavage face etched 30 sec in Moran's NaCl etchant showing edge of specimen to establish orientation of etch pits.